CM 35239

PATENT SPECIFICATION

NO DRAWINGS

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1,079,553

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The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949, are: — ROGER CHARLE and JEAN GASCON, both citizens of France, of 61, avenue Gavignot, Soisy-sous-Montmorency (Seine et Oise), France and 17, rue Varet, Paris, France and GREGOIRE KALOPISSIS, a citizen of Greece, of 64, rue Vauvenargues, Paris, France.

COMPLETE SPECIFICATION

Compositions for Dyeing Keratinic Fibres

We, L'OREAL, a French Body Corporate of 14 Rue Royale, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to new compositions for use in dyeing hair and other keratinic fibres.

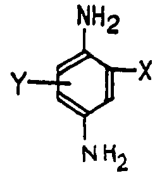
It is known in the dyeing of hair to use primary *para*diamines in conjunction with couplers whereby various shades of colour can be obtained. However, this procedure is not entirely satisfactory, because the colours obtained are not stable and deteriorate substantially on keeping. Moreover, it is not easy to obtain a predetermined shade by reason of the fact that the final shade results from the superimposition of two dyes, namely a first dye obtained by means of the *p*-diamine, which in itself has a dyeing effect, and a second dye obtained by means of the *p*-diamine and the coupler.

It has also been proposed to use solutions which comprise at least one N-disubstituted *p*-diamine and a coupler consisting either of a hydroxylated aromatic derivative, a β-diketone or a pyrazolone derivative, the *p*-diamine and the coupler, taken separately, having only a very low dyeing power, so that the shade obtained results solely from the interaction between the *p*-diamine and the coupler.

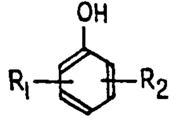
The present invention provides a means of dyeing hair and other keratinic fibres by the conjoint use of *p*-diamines and certain couplers which produce dyestuffs that have exceptional stability to light for periods of the order of 12 months, which is an ample time with regard to the dyeing of human hair.

On the other hand, although the *p*-diamines of this invention are capable when used alone, of forming an intense coloration which may range from light brown to black, their association with the couplers of the invention brings about a much more rapid formation of dyestuffs than when the *p*-diamine is used alone. Consequently, the formation of the browns due to the *p*-diamine is insignificant as compared with the formation of the dye obtained by the *p*-diamine-coupler association, and the final shade obtained depends upon this dye and not on the combination of two separate dyes.

The dyeing compositions of the invention comprise at least one compound of formula (I) and at least one coupler of formula (II), (III) or (IV), the formula (I) being:



in which X and Y, which can be the same or different, each represent hydrogen, halogen, alkyl or alkoxy; Y being attached at any one of the free positions;
formula (II) being:



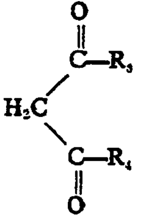
in which

R_1 represents —OCH_3 in the 4-position and R_2 represents H, —CH_3 or —$NHCOCH_3$ in the 2-position, or

R_2 represents H or —CH_3 in the 6-position and R_1 in the 3-position is represented by: —CH_3, —OCH_3, —$NHCOCH_3$, —$NHCH_2CONH_2$, —$NHCH_2CON(C_2H_5)_2$, —$NHCOCH_2N(CH_3)_2$ or —$NHCOCH_2N(C_2H_5)_2$,

or R_2 represents —CH_3 in the 6-position and R_1 represents a halogen in the 3- or 5-position;

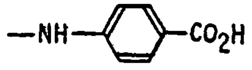
formula (III) being:



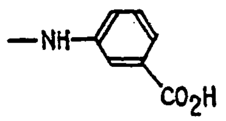
in which R_3 and R_4 are both —CH_3, or

R_3 represents —CH_3 and R_4 represents —OC_2H_5, or

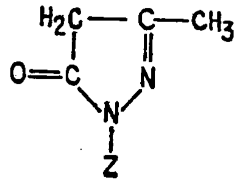
R_3 represents phenyl and R_4 represents



or



and formula (IV) being:



in which:

Z represents a phenyl, 3-sulphophenyl, 4-sulphophenyl or 2-chloro-5-sulphophenyl radical.

In formula (I) where X or Y is an alkyl or alkoxy radical it is preferably methyl, methoxy, ethyl or ethoxy; and where X or Y is halogen it is preferably chlorine.

An essential feature of the invention is that the molar ratio of p-diamine to coupler is less than 1.

The dye compositions of the invention are conveniently used in the form of aqueous solu- having a pH of from 6 to 10. The compositions can contain dyestuffs other than those of the invention, for instance ones which may be used under the same conditions as direct dyestuffs, for example azo dyestuffs, or dyestuffs produced, in accordance with our Specification No. 31,109/64 (Serial No. 1,025916), of from the same couplers and an N-disubstituted p-diamine. The compositions can also contain wetting agents, dispersing agents, penetration agents and other ingredients generally employed for hair dyeing.

The dyeing solutions according to the invention provide a wide range of shades. Thus, use of couplers of formula (II) gives blue shades, couplers of the formula (III) gives yellow shades and couplers of the formula (IV) give red shades. Moreover it is possible by using mixtures of two couplers belonging to the formulae (II), (III) or (IV) in various proportions, with the p-diamine, to obtain all shades lying between the colours obtained when each of the couplers is used alone with the p-diamine.

In other words, it will be seen that, by using a limited number of p-diamines and couplers of the invention it is possible by choosing suitable pairs of p-diamines and couplers, and if desired simultaneously using a number of couplers, to obtain a whole range of shades suitable for hair dyes.

Moreover, the dyes formed by the dye solutions have been found to be exceptionally resistant to ageing with no chemical evolution of the dyeing products obtained.

The present invention also provides a method of dyeing hair or other keratinic fibres which comprises applying to the keratinic fibres a compound of formula (I) and a coupler of formula (II), (III) or (IV), allowing sufficient time to elapse for the compounds applied to exert their dyeing effect, and then removing from the keratinic fibres any unwanted excess of the compounds, e.g. by rinsing, shampooing, washing and drying. It will be understood that, as is usual when p-diamine dyes are used, hydrogen peroxide or like oxidising agent will be also applied to the fibres. The compounds may suitably be applied to the hair in the form of a composition of the invention to which has been added the oxidising agent. Alternatively, the p-diamine and coupler may be applied separately to the hair, the oxidising agent being applied together with one of them.

The invention is illustrated by the following Examples.

EXAMPLE 1

There is prepared a solution containing:

diamine:		
1,2-dimethyl-3,6-diaminobenzene	1.02	g
coupler:		
2,5-dimethylphenol	1.22	g
solvent:		
ethyl alcohol	5	cc
sodium hydroxide	0.02	g
ammonia solution (22° Bé)	6	cc
water, q.s. for	50	cc

This solution, which may be kept, is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.2.

The mixture is then applied to white hair for 20 to 30 minutes. After shampooing, the hair is rinsed and dried. There is obtained a greyish purple-blue shade.

EXAMPLE 2

There is prepared a solution containing:

diamine:		
1,2-dimethyl-3,6-diaminobenzene	1.02	g
coupler:		
4-N-benzoylacetaminobenzoic acid	9	g
solvent:		
Ammonia solution (22° Bé)	12	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of hydrogen peroxide (6%). The pH is 9.0.

The mixture is then applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, a medium yellow shade is obtained.

EXAMPLE 3

There is prepared a solution containing:

diamine:		
1,2-dimethyl-3,6-diaminobenzene	1.02	g
coupler:		
1-phenyl-3-methyl-5-pyrazolone	1.3	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of hydrogen peroxide (6%). The pH is 9.5.

The mixture is then applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, there is obtained a light greyish-red shade.

The application of said mixture on yack hair produces the same tint.

EXAMPLE 4

There are mixed, in any proportions, a mixture of a solution having the composition given in Example 1 and a solution having the composition given in Example 2. An equal volume of hydrogen peroxide (6%) is then added, and the mixture is applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, there is obtained, depending upon the proportions of the two solutions of Examples 1 and 2 employed, shades ranging from greyish purple-blue to medium yellow, passing through the greens.

EXAMPLE 5

A solution having the composition given in Example 2 and a solution having the composition given in Example 3 are mixed in any proportions. An equal volume of hydrogen peroxide (6%) is then added, and the mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, there is obtained, depending upon the proportions in which the solutions of Examples 2 and 3 are employed, shades ranging from medium yellow, through shades of orange to faint greyish-red.

EXAMPLE 6

A solution having the composition given in Example 3 and a solution having the composition given in Example 1 are mixed in any proportions. An equal volume of hydrogen peroxide (6%) is added, and the mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a dyeing effect ranging from faint greyish-purple-blue, passing through the purple shades, is obtained.

EXAMPLE 7

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.61	g
coupler:		
5-chloro-2-methylphenol	1.95	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.02	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of hydrogen peroxide (6%). The pH is 9.2.

The mixture is applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, a dark greenish-blue tint is obtained.

EXAMPLE 8

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.61	g
coupler:		
3-chloro-2-methylphenyl	1.95	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.02	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.2.

The mixture is applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, a blueish-green shade is obtained.

EXAMPLE 9

There is prepared a solution containing:

diamine:		
2,5-diamino-4-methoxytoluene	0.30	g
coupler:		
3-N-carbamylmethylaminophenol	2	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.6.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a dark purplish-grey shade is obtained.

EXAMPLE 10

There is prepared a solution containing:

diamine:

2,5-diaminoanisole	0.24	g
coupler:		
3 - N - (N′ - diethylcarbamylmethyl) - aminophenol	0.36	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.6.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a dark violet shade is obtained.

EXAMPLE 11

There is prepared a solution containing:

diamine:		
4-chloro-2,5-diaminotoluene	0.78	g
coupler:		
2 - methyl - 5 - N - carbamylmethylaminophenol	2.36	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.6.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a greyish purple-red shade is obtained.

EXAMPLE 12

There is prepared a solution containing:

diamine:		
2,5-diamino-4-methoxytoluene	0.3	g
coupler:		
2 - methyl - 5 - N - (N′ - diethylcarbamylmethyl)-aminophenol	0.5	g
solvent:		
Sodium hydroxide	0.04	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.9.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, there is obtained a greyish reddish-purple shade.

EXAMPLE 13

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.61	g
coupler:		
4-methoxyphenol	0.45	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.02	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.3.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed, and dried, there is obtained a dark blue shade.

EXAMPLE 14

There is prepared a solution containing:

diamine:		
2,5-diamino-4-methoxytoluene	0.61	g
coupler:		
2-methyl-4-methoxyphenol	0.50	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.02	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.3.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed, and dried, a dark blue shade is obtained.

EXAMPLE 15

There is prepared a solution containing:

diamine:		
1,4-diaminobenzene hydrochloride	0.18	g
coupler:		
2-acetamino-4-methoxyphenol	0.18	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.4.

This mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a dark blue shade is obtained.

EXAMPLE 16

There is prepared a solution containing:

diamine:		
1,3-dimethyl-2,5-diaminobenzene	1.02	g
coupler:		
2-methyl-5-acetaminophenol	2.0	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of hydrogen peroxide (6%). The pH is 9.6.

This mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a greyish purple-blue shade is obtained.

EXAMPLE 17

There is prepared a solution containing:

diamine:		
1,3-dimethyl-2,5-diaminobenzene	1.02	g
coupler:		
1 - phenyl - 3 - methyl - 5-pyrazolone - 3′ - sulphonic acid	2	g
solvent:		
Ammonia solution (22° Bé)	8	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of hydrogen peroxide (6%). The pH is 9.7.

This mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a faint reddish-brown shade is obtained.

EXAMPLE 18

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.61	g
coupler:		
3-acetaminophenol	2.25	g
solvent:		
a) water (the pH is 6.4), or	50	cc
b) NaHCO$_3$ solution (1.70 g/l) (the pH is 6.9), or	50	cc
c) Na$_2$CO$_3$ solution (2.12 g/l) (the pH is 8.4)	50	cc

Each of these three solutions is mixed with an equal volume of 6% hydrogen peroxide.

Each mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a blueish-black shade is obtained in each of the three cases.

EXAMPLE 19

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.61	g
coupler:		
3-acetaminophenol	2.25	g
solvent:		
Aqueous solution of NH$_3$ (24 g/l) (the pH is 9.5)	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide.

This mixture is applied to white hair for 20 to 30 minutes. After the hair has been washed, rinsed and dried, a dark greyish-blue shade is obtained.

EXAMPLE 20

There is prepared a solution A containing:

3-β-(N'-diethylamino)acetaminophenol	1.11	g
ammonia solution (22° Bé)	6	cc
water q.s. for	100	cc

There is prepared a solution B containing:

2,5-diaminotoluene	0.25	g
hydrogen peroxide (20 vol)	50	cc
water q.s. for	100	cc

White hair is treated with solution A and, after 20 minutes, the hair is rinsed and treated with solution B. After application for 20 minutes, the hair is washed, rinsed and dried. The dyeing effect obtained has a greenish-grey shade

EXAMPLE 21

There is prepared a solution A containing:

2 - methyl - 5 - β - (N' - dimethyl)-aminoacetaminophenol	1.18	g
ammonia solution (22° Bé)	6	cc
water q.s. for	100	cc

There is prepared a solution B containing:

4-methoxy-2,5-diaminotoluene	0.3	g
ammonia solution (22° Bé)	6	cc
hydrogen peroxide (20 vol)	50	cc
water q.s. for	100	cc

White hair is treated with solution A and, after 20 minutes, the hair is rinsed and treated with solution B. After application for 20 minutes, the hair is washed, rinsed and dried. The dyeing effect obtained has a pale green shade

EXAMPLE 22

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.15	g
coupler:		
3-N-benzoylacetaminobenzoic acid	0.5	g
solvent:		
Ammonia solution (22° Bé)	12	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of hydrogen peroxide (6%). The pH is 9.

This mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, a medium yellowish-brown dyeing effect is obtained.

EXAMPLE 23

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.75	g
coupler:		
1 - phenyl - 3 - methyl - 5-pyrazolone - 4' - sulphonic acid	1.45	g
solvent:		
Ammonia solution (22° Bé)	8	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.5.

This mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, there is obtained a dark reddish-brown dyeing effect.

EXAMPLE 24

There is prepared a solution containing:

diamine:		
1,2-dimethyl-3,6-diaminobenzene	1.02	g
coupler:		
2' - chloro - 1 - phenyl - 3-methyl - 5 - pyrazolone - 5'-sulphonic acid	2.1	g
solvent:		
Ammonia solution (22° Bé	8	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.5.

This mixture is applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, there is obtained a medium brown shade.

EXAMPLE 25

There is prepared a solution containing:

diamine:

2,5-diamino-4-methoxytoluene	0.6	g
coupler:		
Ethyl acetylacetate	5	g
solvent:		
Ammonia solution (22° Bé)	12	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.5.

This mixture is applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, a medium yellow dyeing effect is obtained.

EXAMPLE 26

There is prepared a solution containing:

diamine:		
2,5-diaminotoluene	0.25	g
coupler:		
Acetylacetone	2.5	g
solvent:		
Ammonia solution (22° Bé)	12	cc
Water, q.s. for	50	cc

This solution is mixed with an equal volume of 6% hydrogen peroxide. The pH is 9.0.

This mixture is applied to white hair for 20 to 30 minutes. After washing, rinsing and drying, there is obtained a medium olive-brown shade.

If a similar solution containing no coupler is employed, a yellowish-greyish brown shade is obtained.

EXAMPLE 27

There is prepared a solution A containing:

diamine:		
1,3-dimethyl-2,5-diaminobenzene	0.68	g
coupler:		
2,5-dimethylphenol	1.22	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.2	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

There is thereafter prepared a solution B containing:

diamine:		
[4 - amino - 3 - methyl - N - β-sulphamidoethyl - aniline] sulphate	1.40	g
coupler:		
2,5-dimethylphenol	1.22	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.2	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

Solutions A and B are mixed in any proportions, and there is added to this mixture an equal volume of 6% hydrogen peroxide. The pH is 9.6.

This mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, there are obtained, depending upon the proportions in which solutions A and B are employed, dyeing effects ranging from deep purple-blue to medium greenish-blue.

EXAMPLE 28

There is prepared a solution A containing:

diamine:		
2,5-diaminotoluene	0.61	g
coupler:		
3-acetaminophenol	2.2	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

There is prepared a solution B containing:

diamine:		
1,2-dimethyl-3,6-diaminobenzene	1.02	g
coupler:		
3-acetaminophenol	2.2	g
solvent:		
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

Solutions A and B are mixed in any proportions, and there is added to the mixture obtained an equal volume of 6% hydrogen peroxide. The pH is 9.5.

The mixture is then applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, there is obtained a dyeing effect ranging from dark yellowish-blue to dark greenish-blue, depending upon the proportions of A and B.

EXAMPLE 29

There is prepared a solution A containing:

diamine:		
1,3-dimethyl-2,5-diaminobenzene	0.68	g
coupler:		
2,5-dimethylphenol	1.22	g
solvent:		
Ethyl alcohol	5	cc
Sodium hydroxide	0.2	g
Ammonia solution (22° Bé)	6	cc
Water, q.s. for	50	cc

There is prepared a solution B containing:

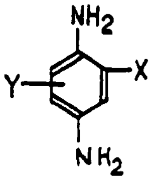
2,4,4'-trihydroxyazobenzene	0.5	g
Sodium hydroxide	0.08	g
Water, q.s. for	50	cc

These two solutions A and B are mixed. This mixture is applied to white hair for 20 to 30 minutes. When the hair has been washed, rinsed and dried, there is obtained, depending upon the proportions in which the two solutions A and B have been used, dyeing effects which range from deep purplish-blue to bright yellow, passing through shades of dark green.

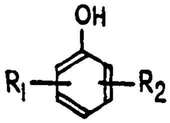
When the dyeing test of the Examples was applied to yak hair, the same shades were obtained as in the tests on human hair.

WHAT WE CLAIM IS:—

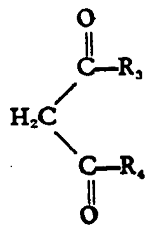
1. A composition for use in dyeing keratinic fibres, comprising at least one *p*-diamine of formula (I) and at least one coupler of formula (II), (III) or (IV), the formula (I) being:



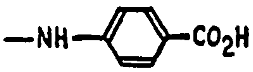
in which X and Y, which can be the same or different, each represent hydrogen, halogen, alkyl or alkoxy; formula (II) being:



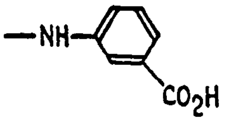
in which
R_1 represents $-OCH_3$ in the 4-position and R_2 represents H, $-CH_3$ or $-NHCOCH_3$ in the 2-position, or
R_2 represents H or $-CH_3$ in the 6-position and R_1 in the 3-position is represented by: $-CH_3$, $-OCH_3$, $-NHCOCH_3$, $-NHCH_2CONH_2$, $-NHCH_2CON(C_2H_5)_2$, $-NHCOCH_2N(CH_3)_2$ or $-NHCOCH_2N(C_2H_5)_2$, or
R_2 represents $-CH_3$ in the 6-position and R_1 represents a halogen in the 3- or 5-position; formula (III) being:



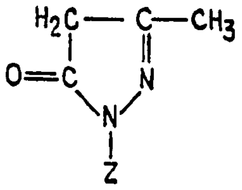
in which R_3 and R_4 are both $-CH_3$, or R_3 represents $-CH_3$ and R_4 represents $-OC_2H_5$, or
R_3 represents phenyl and R_4 represents



or



and formula (IV) being:



in which:
Z represents a phenyl, 3-sulphophenyl, 4-sulphophenyl or 2-chloro-5-sulphophenyl radical, the molar ratio of *p*-diamine to coupler being less than 1.

2. A composition according to claim 1, in which the *p*-diamine is 1,2-dimethyl-3,6-diaminobenzene, 2,5-diaminotoluene, 2,5-diamino-4-methoxytoluene, 2,5-diaminoanisole, 4 - chloro - 2,5 - diaminotoluene, 1,4 - diaminobenzene hydrochloride or 1,3-dimethyl-2,5-diaminobenzene.

3. A composition according to claim 1 or 2, in which the said coupler is 2,5-dimethylphenol, 5 chloro - 2 - methylphenol, 3-chloro - 2 - methylphenol, 3 - N - carbamylmethylaminophenol, 3 - N - (N′ - diethylcarbamylmethyl) - aminophenol, 2 - methyl-5 - N - carbamylmethylaminophenol, 4-methoxyphenol, 2 - methyl - 4 - methoxyphenol, 2 - acetamino - 4 - methoxyphenol, 2 - methyl - 5 - acetaminophenol, 3 - acetaminophenol, 3 - β - (N′ - diethylamino)-acetaminophenol or 2 - methyl - 5 - β - (N′-dimethyl)aminoacetaminophenol.

4. A composition according to claim 1 or 2, in which the said coupler is 4-N-benzoylacetaminobenzoic acid, 3-N-benzoylacetaminobenzoic acid, ethyl acetylacetate or acetyl acetone.

5. A composition according to claim 1 or 2, in which the said coupler is 1 - phenyl - 3-methyl - 5 - pyrazolone, 1 - phenyl - 3-methyl - 5 - pyrazolone - 3′ - sulphonic acid or 1 - phenyl - 3 - methyl - 5 - pyrazolone-4′ - sulphonic acid, 2′ - chloro - 1 phenyl - 3-methyl - 5 - pyrazolone - 5′ - sulphonic acid.

6. A composition according to any of the preceding claims, which is in the form of an aqueous solution having a pH in the range 6 to 10.

7. A composition according to any of the preceding claims, which contains a dyestuff other than one of formula (I).

8. A composition according to any of the preceding claims, which contains a surface active agent.

9. A composition according to claim 1, substantially as described herein.

10. A composition for use in dyeing keratinic fibres, comprising a compound of formula (I) and a coupler of formula (II), (III) or (IV) substantially as described in any of the Examples.

11. A method of dyeing hair or other kera-

tinic fibres, which comprises applying to the keratinic fibres a p-diamine of formula (I) and a coupler of formula (II), (III) or (IV), the molar ratio of p-diamine to coupler being less than 1, allowing sufficient time to elapse for the compounds applied to exert their dyeing effect and then removing from the keratinic fibres any unwanted excess of said compounds.

12. A method according to claim 11, in which hydrogen peroxide or a like oxidising agent is applied to the hair with one of said compounds.

13. A method according to claim 11, substantially as described herein.

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